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(54) ELECTROLYZED MANGANESE DIOXIDE, ITS PRODUCTION AND MANGANESE DRY CELL

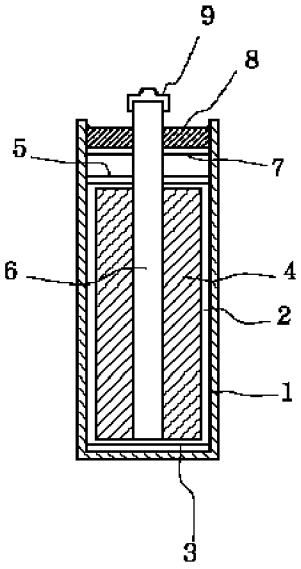
(57)Abstract:
PROBLEM TO BE SOLVED: To provide electrolyzed manganese dioxide capable of suppressing reactive property of electrolyzed manganese dioxide used as a positive electrode material of a manganese dry cell with electroconductive acetylene black, especially electroconductive acetylene black having 70-250m2/g BET specific surface area and improving initial properties and storing properties, to provide its producing method and to provide a manganese dry cell using the electrolyzed manganese dioxide as a positive electrode active material.
SOLUTION: This electrolyzed manganese dioxide has 1.90-1.96 X-value of MnOx, ≥1.5wt.% content of attached water measured by JIS and ≥3.0wt.% content of bound water eliminating within the range of 120-400°C measured by a gravimetric method. The second objective manganese dry cell is obtained by mixing the electrolyzed manganese dioxide with an electrolysis solution mainly composed of electroconductive acetylene black, preferably electroconductive acetylene black having 70-250m2/g BET specific surface are

and zinc chloride or ammonium chloride, and used as a positive electrode mixed agent.

JAPANESE [JP,09-188519,A]

[Translation done.]

Drawing selection Drawing 1



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CLAIMS

[Claim(s)]
[Claim 1]A manufacturing method of electrolytic manganese dioxide heating powdered or massive electrolytic manganese dioxide after electrolysis in solution on 50-100 ** conditions under alkaline ammonium compound coexistence which reacts to sulfuric acid after the time of neutralization, or neutralization.
[Claim 2]Electrolytic manganese dioxide, wherein absorbed water content from which it is obtained by a manufacturing method of claim 1, and attached groundwater content according [an X value of MnO_x] to 1.90-1.96, and JIS measurement is desorbed in [by a weight method] 120-400 ** 1.5% of the weight or more is 3.0 % of the weight or more.

[Claim 3]A manganese dry battery which prepares conductive acetylene black, zinc chloride, or ammonium chloride with an electrolysis solution made into a subject, and uses electrolytic manganese dioxide according to claim 2 as positive electrode mixture.
[Claim 4]The manganese dry battery according to claim 3 whose BET specific surface area of said conductive acetylene black is 70-250m^2/g.

[Translation done.]

JAPANESE [JP,09-188519,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION TECHNICAL PROBLEM MEANS EXAMPLE DESCRIPTION OF DRAWINGS DRAWINGS

[Translation done.]

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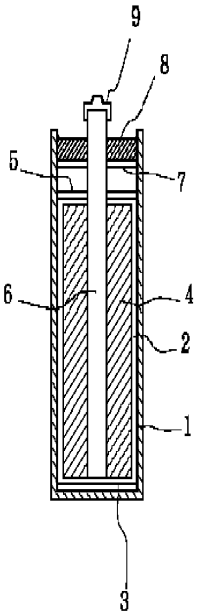
DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]Electrolytic manganese dioxide in which this invention has the shape of specificity, and a manufacturing method for the same, And it is related with the manganese dry battery which uses it preparing conductive acetylene black, zinc chloride, or ammonium chloride conductive acetylene black, especially whose BET specific surface area are 70-250m^2/g about this electrolytic manganese dioxide with the electrolysis solution made into a subject, and carrying out positive electrode mixture.
[0002]
[Description of the Prior Art]The manganese dry battery using the solution which considered it as the zinc alloy as negative electrode active material by having considered it as electrolytic manganese dioxide as positive active material, and used zinc chloride or ammonium chloride as the main ingredients as an electrolysis solution is known well.
[0003]As a conventional manufacturing method of electrolytic manganese dioxide used for the anode of this manganese dry battery, for example after the electrolysis process, water or warm water washes and neutralizes and electrolytic manganese dioxide has been obtained. The manganese dry battery which used these electrolysis diacid-

Drawing selection Drawing 1



[Translation done.]

ized comics for the anode reacted between electrolytic manganese dioxide and conductive acetylene black during that preservation, and since the choke damp was generated, there was a problem that characteristic degradation increased as internal resistance rose and the retention period was prolonged during discharge. Since this tendency was further accelerated on load discharging conditions with being required [much] of a dry cell in recent years, solution of this problem had become pressing need.

[0004]In recent years, in order to raise the load discharging characteristic of a manganese dry battery, the trial which raises the capability to carry out absorption maintenance of the electrolysis solution required for the discharge reaction of electrolytic manganese dioxide is also made using conductive acetylene black with larger specific surface area than before, but. There is a problem that conductive acetylene black with such big specific surface area has still higher reactivity with electrolytic manganese dioxide.

[0005]Reactant low conductive acetylene black with electrolytic manganese dioxide of the solution retention of an electrolysis solution is insufficient, and a heavy loading characteristic falls. For this reason, although electrolytic manganese dioxide could be heated in the air and reactivity could also be lowered, reduction of very important attached groundwater arose on the discharge characteristic of a manganese dry battery, especially, by heating at not less than 100 **, even absorbed water was lost and there was a problem that the initial characteristic of a dry cell itself deteriorated notably.

[0006]As others, if electrolytic manganese dioxide is kept extremely for a long period of time, the reactivity with conductive acetylene black will be controlled, but it is difficult to provide such electrolytic manganese dioxide industrially.

[0007]

[Problem(s) to be Solved by the Invention]Electrolytic manganese dioxide and conductive acetylene black by which this invention is used for the positive electrode material of a manganese dry battery, Reactivity with conductive acetylene black of 70-250 m of BET specific surface area ^{2}/g is controlled especially, It aims at providing electrolytic manganese dioxide which can improve an initial characteristic and a conservation characteristic, a manufacturing method for the same, and the manganese dry battery using this electrolytic manganese dioxide as positive active material.

[0008]

[Means for Solving the Problem]In order to reduce gas volume generated during preservation of a manganese dry battery, as a result of this invention persons' repeating examination wholeheartedly in view of such a situation. Under alkaline ammonium compound coexistence which reacts powder or massive electrolytic manganese dioxide after electrolysis to sulfuric acid, By heating in solution, moisture (attached groundwater and absorbed water content) of electrolytic manganese dioxide, Electrolytic manganese dioxide which is comparable as electrolytic manganese dioxide by a conventional method, and has an X value of MnO_X in the range of 1.90-1.96 is manufactured, The conventional BET specific surface area prepares conductive acetylene black, zinc chloride, or ammonium chloride which is a 60-m^2/g grade with an electrolysis solution made into a subject, and considers it as positive electrode mixture, The knowledge of improvement in a conservation characteristic being accepted if this is used for a manganese dry battery is carried out, If a BET specific surface area prepares with a thing of 70-250-m^2/g, considers it as positive electrode mixture and furthermore uses this for a manganese dry battery as conductive acetylene black, An initial characteristic is improved, and it finds out that a highly efficient manganese dry battery which was

moreover excellent in a conservation characteristic can be manufactured, and came to complete this invention.
[0009]That is, this invention is in a manufacturing method of electrolytic manganese dioxide heating powdered or massive electrolytic manganese dioxide after electrolysis in solution on 50-100 ** conditions under alkaline ammonium compound coexistence which reacts to sulfuric acid after the time of neutralization, or neutralization.
[0010]This invention has an X value of MnO_X in electrolytic manganese dioxide, wherein absorbed water content from which attached groundwater content by 1.90-1.96, and JIS measurement is desorbed in [by a weight method] 120-400 ** 1.5% of the weight or more is 3.0 % of the weight or more.
[0011]This invention above-mentioned electrolytic manganese dioxide Conductive acetylene black, A manganese dry battery which a BET specific surface area prepares conductive acetylene black, zinc chloride, or ammonium chloride of 70-250-m^2/g with an electrolysis solution made into a subject, and uses as positive electrode mixture preferably.
[0012]
[Embodiment of the Invention]Hereafter, it explains still in detail about this invention. The choke damp is emitted by the reaction of electrolytic manganese dioxide in positive electrode mixture, and conductive acetylene black as one of the causes of the characteristic degradation after preservation of a manganese dry battery, and the internal pressure of a cell rises, In order to reduce the adhesion between a negative-electrode separator and positive electrode mixture, it is thought that reaction efficiency is worsened.
[0013]It is important that the moisture (attached groundwater and absorbed water content) of electrolytic manganese dioxide is fully maintained in order not to degrade the initial characteristic of a cell, and the X value of MnO_X is in a fixed range.
[0014]In [as a result of repeating examination per / which satisfies the above-mentioned conditions / electrolytic manganese dioxide paying attention to such a fact] the product processing process of manganese dioxide after electrolysis, The alkaline ammonium compound reacted to sulfuric acid was added the time of neutralization, or after neutralization, and it found out that electrolytic manganese dioxide which can solve an aforementioned problem could be manufactured by heating in solution under 50-100 ** conditions. Hereafter, heating in solution is called water heat treatment.
[0015]. This reacts to conductive acetylene black easily by the mutual reaction with each oxidizing degree in electrolytic manganese dioxide of a manganic acid ghost. It is the thing where a high order manganic acid ghost reacts to a low-grade oxide, and both oxides unnecessary for a discharge reaction are removed, which does not have degradation of the initial battery characteristic and which was able to obtain electrolytic manganese dioxide which was moreover excellent in the conservation characteristic, Although a reaction mechanism is not clear, in the process in which the alkaline ammonium compound reacted to sulfuric acid reacts to the sulfate ion which exists in electrolytic manganese dioxide by a high temperature state, it is thought that the catalytic role which accelerates the mutual reaction shown below is played.
[0016]
[Formula 1]

$$MnO_x + MnO_y \rightarrow 2MnO_2 \qquad x + y = 4,\ x > y$$

[0017]As an alkaline ammonium compound reacted to these sulfuric acid, ammonium hydroxide, ammonium

carbonate, ammonium acid carbonate, etc. are mentioned. Although manufacture of electrolytic manganese dioxide which can control reactivity with conductive acetylene black with heating in the atmosphere is also possible under an ammonium compound or ammonium ion coexistence, In this case, since it is necessary to maintain moisture (attached groundwater and absorbed water content) of electrolytic manganese dioxide used as a factor important for a discharge characteristic, Since equipment and the cleanup cost are high as a method of it being necessary to maintain a steam partial pressure under heating highly, and processing a lot of electrolytic manganese dioxide industrially, it is not desirable.

[0018]That namely, water-heat-treatment temperature was 50-100 ** on the electrolytic manganese dioxide manufacturing conditions of this invention for which degradation of a conservation characteristic was controlled, maintaining an initial discharge characteristic, When manufacturing electrolytic manganese dioxide on a scale of industrial, at less than 50 **, take too much time which processing takes, and the temperature leads to a steep rise of energy cost at more than 100 **, and. Since solubility to water of ammonium ion falls and an evaporation loss increases, in economical efficiency, it is not realistic. It is 80-90 ** desirably as conditions for water-heat-treatment temperature.

[0019]Thus, absorbed water content in which attached groundwater content according [an X value of MnO_X] to 1.90-1.96, and JIS measurement is desorbed from obtained manganese dioxide in [by a weight method] 120-400 ** 1.5% of the weight or more is 3.0 % of the weight or more. An initial discharge characteristic falls that this X value is less than 1.90. This is considered to be because for there to be little content of the MnO_2 required for a discharge reaction itself and for content of a lower-grade oxide which is not contributed to discharge to also have it. [much] Since a high order oxide remains when X values are 1.96 **, reactant control with conductive acetylene black is insufficient. When attached groundwater content is less than 1.5 % of the weight and absorbed water content is less than 3.0 % of the weight, an initial discharge characteristic all falls.

[0020]If a BET specific surface area of conductive acetylene black exceeds 250-m^2/g, although an initial discharge characteristic will improve, a survival rate after preservation of a manganese dry battery deteriorates, and a fall of a discharge characteristic after preservation is brought about. A survival rate expresses discharging duration after preservation when discharging duration immediately after manufacture is made into 100% in units of percentage here.

[0021]Electrolytic manganese dioxide of the shape of such specificity Conductive acetylene black, When especially a BET specific surface area prepares acetylene black, zinc chloride, or ammonium chloride of 70-250-m^2/g with an electrolysis solution made into a subject and considers it as positive electrode mixture, a manganese dry battery of this invention with which a conservation characteristic and an initial discharge characteristic have been improved simultaneously is obtained.

[0022]

[Example]Hereafter, an example and a comparative example explain this invention in detail.

In example 1 sulfate bath, current density 70 A/m^2, 90 ** (fixed) of electrolysis solution temperature, With 90 ** and 5 l. of hot water, after 30-minute washing, the decantation was carried out, with further tales doses of water, it agitated, what carried out coarse grinding of 3 kg of electrolytic manganese dioxide to which electrolytic deposition of the mole ratio of the manganese/sulfuric acid in an electrolysis solution was carried out on the conditions set to 1.5

was washed for 24 hours, and the decantation was carried out again. It pulverized so that water heat treatment of electrolytic manganese dioxide obtained here might be carried out for 32 hours, stoving might be carried out at 40 more ** 90 ** after neutralization for 1 hour so that JIS pH of electrolytic manganese dioxide may be set to 5.5 with ammonium carbonate, and mean particle diameter might be set to about 25 micrometers, and electrolytic manganese dioxide was obtained.

[0023]R6 manganese dry battery shown in drawing 1 by using this electrolytic manganese dioxide as positive active material was made as an experiment. The 300-mA continuous discharge examination (final voltage 0.9V) after the 20 ** early stages of this cell, and 45 ** and one-month preservation was done, and the result was shown in Table 1. in the figure -- 1 -- Zn can (negative electrode) and 2 -- a separator and 3 -- a bottom paper and 4 -- a carbon rod and 7 show a top cover, 8 shows an obturation agent, and, as for an overlay and 6, positive electrode mixture and 5 show an anode cap 9, respectively.

[0024]Electrolytic manganese dioxide used as positive active material in order to double the electrolytic manganese dioxide weight used for one R6 manganese dry battery here, The compounding weight ratio of conductive acetylene black was as being shown in Table 1, the electrolysis solution was produced by the ratio as for which 30 % of the weight of zinc chloride and 70 % of the weight of water become, and zinc chloride used the thing of specific gravity 1.53 47.6% of the weight. As for conductive acetylene black, the BET specific surface area used the thing of 70-m^2/g here. The compounding ratio of electrolytic manganese dioxide, conductive acetylene black, and an electrolysis solution is illustration, and adjusting suitably according to battery structure is possible.

[0025]In an example disulfuric acid bath, current density 50 A/m^2, 95 ** (fixed) of electrolysis solution temperature, The same product processing as Example 1 is performed for electrolytic manganese dioxide to which electrolytic deposition of the mole ratio of the manganese/sulfuric acid in an electrolysis solution was carried out on the conditions set to 1.5, And it pulverized so that 90 ** and 12-hour water heat treatment might be performed after neutralization, and stoving might be carried out at 40 more ** for 1 hour, using ammonium hydroxide as an alkaline ammonium compound and mean particle diameter might be set to about 25 micrometers, and electrolytic manganese dioxide was obtained.

[0026]Using this electrolytic manganese dioxide, R6 manganese dry battery was made as an experiment by the same method as Example 1, and the spark test was done. A result is shown in Table 1. The BET specific surface area as Example 1 with the same conductive acetylene black used the thing of 70-m^2/g here.

[0027]In example 3 sulfate bath, current density 60 A/m^2, 95 ** (fixed) of electrolysis solution temperature, The same product processing as Example 1 is performed for electrolytic manganese dioxide to which electrolytic deposition of the mole ratio of the manganese/sulfuric acid in an electrolysis solution was carried out on the conditions set to 1.0, And it pulverized so that 90 ** and 20-hour water heat treatment might be performed after neutralization, and stoving might be carried out at 40 more ** for 1 hour, using ammonium hydroxide as an alkaline ammonium compound and mean particle diameter might be set to about 25 micrometers, and electrolytic manganese dioxide was obtained.

[0028]Using this electrolytic manganese dioxide, except for the compounding weight ratio of electrolytic manganese dioxide in positive electrode mixture, and conductive acetylene black, R6 manganese dry battery was made as an experiment by the same method as Example 1, and the spark test was done. A result is shown in Table 1. The BET specific surface area as Example 1 with the same conductive acetylene black used the thing of 60-m^2/g here.

[0029]The same water heat treatment and product processing as example 4 Example 3 were performed, and electrolytic manganese dioxide was obtained. Using this electrolytic manganese dioxide, R6 manganese dry battery was made as an experiment by the same method as Example 1, and the spark test was done. A result is shown in Table 1. As for conductive acetylene black, the BET specific surface area used the thing of 70-m^2/g here.

[0030]The same water heat treatment and product processing as example 5 Example 3 were performed, and electrolytic manganese dioxide was obtained. Using this electrolytic manganese dioxide, except for the compounding weight ratio of electrolytic manganese dioxide in positive electrode mixture, and conductive acetylene black, R6 manganese dry battery was made as an experiment by the same method as Example 1, and the spark test was done. A result is shown in Table 1. As for conductive acetylene black, the BET specific surface area used the thing of 130-m^2/g here.

[0031]The same water heat treatment and product processing as example 6 Example 3 were performed, and electrolytic manganese dioxide was obtained. Using this electrolytic manganese dioxide, except for the compounding weight ratio of electrolytic manganese dioxide in positive electrode mixture, and conductive acetylene black, R6 manganese dry battery was made as an experiment by the same method as Example 1, and the spark test was done. A result is shown in Table 1. As for conductive acetylene black, the BET specific surface area used the thing of 200-m^2/g here.

[0032]The same water heat treatment and product processing as example 7 Example 3 were performed, and electrolytic manganese dioxide was obtained. Using this electrolytic manganese dioxide, except for the compounding weight ratio of electrolytic manganese dioxide in positive electrode mixture, and conductive acetylene black, R6 manganese dry battery was made as an experiment by the same method as Example 1, and the spark test was done. A result is shown in Table 1. As for conductive acetylene black, the BET specific surface area used the thing of 250-m^2/g here.

[0033]Ammonium hydroxide performed neutralization processing for 3 kg of electrolytic manganese dioxide which carried out electrolytic deposition on the conditions which set the mole ratio of the manganese/sulfuric acid in current density 50 A/m^2, 90 ** (fixed) of electrolysis solution temperature, and an electrolysis solution to 1.5 in the comparative example 1 sulfate bath, and electrolytic manganese dioxide was obtained.

[0034]Using this electrolytic manganese dioxide, except for the compounding weight ratio of electrolytic manganese dioxide in positive electrode mixture, and conductive acetylene black, R6 manganese dry battery was made as an experiment by the same method as Example 1, and the spark test was done. A result is shown in Table 1. As for conductive acetylene black, the BET specific surface area used the thing of 60-m^2/g here.

[0035]The same product processing as the comparative example 2 comparative example 1 was performed, and electrolytic manganese dioxide was obtained. Using this electrolytic manganese dioxide, except for the compounding weight ratio of electrolytic manganese dioxide in positive electrode mixture, and conductive acetylene black, R6 manganese dry battery was made as an experiment by the same method as Example 1, and the spark test was done. A result is shown in Table 1. As for conductive acetylene black, the BET specific surface area used the thing of 200-m^2/g here.

[0036]Using ammonium carbonate as a comparative example 3 alkalinity ammonium compound, 180 ** and 4-hour heat-treatment were performed among the air, and others performed the same product processing as Example 1, and obtained electrolytic manganese dioxide.

[0037]Using this electrolytic manganese dioxide, except for the compounding weight ratio of electrolytic manganese dioxide in positive electrode mixture, and conductive acetylene black, R6 manganese dry battery was made as an experiment by the same method as Example 1, and the spark test was done. A result is shown in Table 1. As for conductive acetylene black, the BET specific surface area used the thing of 130-m^2/g here.

[0038]In comparative example 4 sulfate bath, current density 70 A/m^2, 90 ** (fixed) of electrolysis solution temperature, The same product processing as Example 1 is performed for electrolytic manganese dioxide to which electrolytic deposition of the mole ratio of the manganese/sulfuric acid in an electrolysis solution was carried out on the conditions set to 2.0, And it pulverized so that 95 ** and 48-hour water heat treatment might be performed after neutralization, and stoving might be carried out at 40 more ** for 1 hour, using ammonium hydroxide as an alkaline ammonium compound and mean particle diameter might be set to about 25 micrometers, and electrolytic manganese dioxide was obtained.

[0039]Using this electrolytic manganese dioxide, R6 manganese dry battery was made as an experiment by the same method as Example 1, and the spark test was done. A result is shown in Table 1. As for conductive acetylene black, the BET specific surface area used the thing of 70-m^2/g here.

[0040]In comparative example 5 sulfate bath, current density 50 A/m^2, 95 ** (fixed) of electrolysis solution temperature, The same product processing as Example 1 is performed for electrolytic manganese dioxide to which electrolytic deposition of the mole ratio of the manganese/sulfuric acid in an electrolysis solution was carried out on the conditions set to 1.0, And it pulverized so that 40 ** and 48-hour water heat treatment might be performed after neutralization, and stoving might be carried out at 40 more ** for 1 hour, using ammonium hydroxide as an alkaline ammonium compound and mean particle diameter might be set to about 25 micrometers, and electrolytic manganese dioxide was obtained.

[0041]Using this electrolytic manganese dioxide, R6 manganese dry battery was made as an experiment by the same method as Example 1, and the spark test was done. A result is shown in Table 1. The BET specific surface area as Example 1 with the same conductive acetylene black used the thing of 70-m^2/g here.

[0042]Next, the gas yield investigation examination using each sample, In the deeper container which kept positive electrode mixture at 45 **, after injecting 5 ml of electrolysis solutions into the glass cell for generation-of-gas measurement as shown in drawing 2 for the positive electrode mixture 5g further after an injection, the thing which made the glass cell fill up with a liquid paraffin was immersed, and the gas yield was measured for one week. in addition -- in drawing 2 -- 10 -- positive electrode mixture and 13 show generating gas, 14 shows a constant temperature bath, and, as for a liquid paraffin and 12, a micropipette and 11 show warm water (fixed 45 **) 15, respectively.

[0043]Positive electrode mixture was produced by the same method as the time of R6 manganese-dry-battery manufacture described previously, and used what also has the same electrolysis solution and conductive acetylene black. The gas yield of each sample is shown in Table 1 with R6 manganese-dry-battery spark test result. The analysis result of the moisture of each sample and the X value of MnO_X was similarly shown in Table 1.

[0044]

[Table 1]

実施例・比較例	MnO_2のX値	水分（%）		導電性アセチレンブラックの比表面積（m^2/g）	＊1 M：C	300mA連続放電持続時間（分）		＊2 残存率（%）	＊3 ガス発生量の相対値
		付着水（RT～107℃）	結合水（120～400℃）			20℃初期	45℃×1ヶ月保存		
実施例1	1.90	2.3	3.4	70	7：1	77	65	84	60
実施例2	1.96	2.3	3.4	70	7：1	78	65	83	62
実施例3	1.93	2.3	3.4	60	6：1	72	63	88	66
実施例4	1.93	2.3	3.4	70	7：1	79	58	73	69
実施例5	1.93	2.3	3.4	130	10：1	81	57	70	72
実施例6	1.93	2.3	3.4	200	11：1	82	53	65	75
実施例7	1.93	2.3	3.4	250	12：1	84	51	61	80
比較例1	1.97	2.3	3.4	60	6：1	74	46	62	100
比較例2	1.97	2.3	3.4	200	11：1	83	35	42	125
比較例3	1.97	0.7	2.9	130	10：1	50	32	64	130
比較例4	1.89	2.3	3.0	70	7：1	51	46	90	43
比較例5	1.97	2.3	3.4	70	7：1	74	47	63	90

＊1：正極合剤中の電解二酸化マンガン（M）と導電性アセチレンブラック（C）の配合重量比とする。
＊2：製造直後の放電持続時間を100とした時の45℃1ケ月保存後の放電持続時間を残存（%）とする。
＊3：45℃、1週間後のガス発生量で、比較例1を100とした指数表示とする。

[0045]It turns out that the discharge characteristic in early stages of 20 ** (immediately after manufacture) falls [x value of MnO_X] by less than 1.90, and the discharge characteristic and survival rate one month after 45 ** are falling by 1.96 ** from Examples 1-2, and 4 and the comparative examples 4-5 so that clearly from the result of this table 1.
[0046]Next, comparison of Examples 3-7 and the comparative example 1 shows the following thing. That is, although the initial characteristic fell a little as compared with the comparative example 1, the improvement in a conservation characteristic was able to plan Example [BET specific surface area / of conductive acetylene black] 3 using 60-m^2/g. Next, the result whose initial characteristic and conservation characteristic of Examples [BET specific surface area / of conductive acetylene black] 4-7 using the range of 70-250-m^2/g are good as compared with the comparative example 1 was obtained. Therefore, as for the specific surface area of conductive acetylene black, for an initial characteristic and a conservation characteristic improving, it is desirable that it is 70-250m^2/g.
[0047]Although the BET specific surface area of an early discharge characteristic of acetylene black improves by 200m^2/g in electrolytic manganese dioxide currently used from the former from the comparative example 2, it turns out that degradation with remarkable survival rate and conservation characteristic is shown.
[0048]In the comparative example 3, it turns out that a battery characteristic and a conservation characteristic fall

[very important attached groundwater] remarkably 0.7% of the weight on the discharge characteristic of a manganese dry battery since absorbed water is as low as 2.9 % of the weight.

[0049]Electrolytic manganese dioxide obtained by water heat treatment according to Example 3, the comparative example 1 and Example 6, and the comparative example 2 inhibits a reaction with conductive acetylene black as compared with conventional electrolytic manganese dioxide, and it turns out that the generation of gas can be suppressed.

[0050]

[Effect of the Invention]If it is used as positive electrode mixture with conductive acetylene black by using as positive active material electrolytic manganese dioxide which has the shape of specificity by this invention, the manganese dry battery which was excellent in the conservation characteristic can be manufactured. If conductive acetylene black of 70-250 m of BET specific surface area ^{2}/g is furthermore used, the manganese dry battery with which not only a conservation characteristic but the initial discharge characteristic has been improved simultaneously can be manufactured.

[Translation done.]